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SOME FEATURES OF POLYMER CRYSTALLIZATION AND MELTING AS EXPOSED BY DTA OF POLY(ETHYLENE ADIPATE)

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An interpretation of all the elements of complex poly(ethylene adipate) DTA curves is given in the light of the ideas developed on the peculiarities of polymer crystallization thermokinetics. Both the amorphized specimens crystallizing during the DTA run, and those pre-crystallized by the tempering of the melt at some fixed temperatures, have been studied. The states of the crystallized polymer differ substantially, depending on whether it is brought to the crystallization temperature from lower or from higher temperatures. The conclusion is drawn that when considering the results of thermal analysis, one must bear in mind the inequality of the nominal and actual crystallization temperatures, as well as the re-crystallization phenomena during melting.

With complex DTA curves the problem arises of assigning their elements to specific acts of absorption or evolution of energy, in the manner adopted, for instance, in optical spectrometry. For crystallizable polymers, such an assignment is in many cases rather difficult to perform. A detailed analysis of the DTA curves is necessary, since a number of peaks may be found in the melting region, even for individual homopolymers.

The problem of the origin of the peak multiplicity is under discussion, the various interpretations given being listed in a recent paper [1]. Those interpretations seem to be preferable in which the polymer state is connected with the crystal formation conditions, as well as with the thermal analysis regime. Due to the realization of various non-equilibrium states and to the relative slowness of the relaxation processes, imperfect crystals are often manifested on the DTA curves as individual phases. The possibility of the co-existence of two crystal types with both folded and extended chains is known to be considered as one of the reasons for the occurrence of double melting peaks. The investigation of poly(ethylene adipate) (PEA), a polymer of rather low molecular weight, enables one to exclude such an interpretation, as formation of folded chain crystals is hardly probable in this case. Polymorphism is considered to be another of the probable reasons of multiplicity. In this respect PEA, exhibiting polymorphic properties, is worthy of investigation.

Some DTA curves for PEA were obtained earlier [2]. A significant feature of these curves is the exothermic maximum preceding the melting peak. As shown somewhat later [3], the crystallization occurring in this temperature range is not connected with the polymorphic transition, at least for specimens crystallized at relatively low temperatures.

However, the detailed interpretation of the PEA DTA curves demanded extension of the experimental material and its treatment on the basis of the ideas developed on the peculiarities of polymer crystallization and melting. The principal starting points of this treatment are as follows:

(a) Consideration of the DTA curve mainly as a characteristic of the alteration of the crystalline-to-amorphous phase ratio in the course of heating in the specific dynamic regime.

(b) Acknowledgement of the fact that the actual temperature of the growth of crystals differs substantially from the nominal temperature of the melt.

(c) Appreciation of the specific crystallization thermokinetics determining the morphology of the crystal formations and giving rise to the compilation of a certain spectrum of crystals, differing in their actual temperature of growth.

(d) Admission that the melting temperature of any crystal of the spectrum mentioned with no re-crystallization is equal to its actual temperature of formation.

(e) Treatment of the role of re-crystallization phenomena resulting in elevation of the melting points and observation of the superposition of melting and re-crystallization processes.

(f) Knowledge of the general rules of mutual state transitions for a dimorphic polymer.

Most of the items cited have already been discussed and motivated [4–6], but the final one will to be explained here in greater detail.

On the transitions in a dimorphic polymer

The proposed scheme of the mutual state transitions of a monotropic dimorph or pseudo-monotropic polymers is a generalization of previous observations [7], which considers the whole set of re-crystallization phenomena, as well as the dependence of each transition upon the temperature and velocity of its alteration [4].

The assignment of a dimorphic polymer to the monotropic or enantiotropic type is known to be rather difficult [8, 9]. In our case it is essential that PEA behaves as a dimorph of monotropic type.

The practically irreversible transition of the low-temperature modification to the high-temperature one ($\beta \rightarrow \alpha$) occurs only at temperatures that are high enough. The kinetics of this process do not generally correspond to re-crystallization kinetics [3]. The superposition of the melting and various crystallization processes during heating makes the DTA curves of PEA rather complicated.

Besides the samples crystallized by exposing the over-cooled melt to isothermal conditions, specimens may be prepared which are crystallized by the "simple" cooling of the melt, i.e. in a dynamic regime, which is most often used in practice. There is good reason to believe that the nature and quantities of the crystalline phases are cooling-rate dependent only inasmuch as the latter determines the duration of passing the temperature regions where each of the forms crystallizes.

It is assumed, for example, that by the fast cooling of a gutta-percha melt, it crystallizes in the β-modification, the α-modification being obtained by slow cooling. However, the point is not at all that each of the modifications requires a definite cooling rate, but merely that in the first case the specimen passes the high-temperature region so quickly that it does not have enough time for crystallization in the α-form. Thus, it has to crystallize at lower temperatures, in the region where the β-modification is formed. In the second case the cooling is so slow that the gutta-percha crystallizes fully at the higher temperatures (in the α-form). Accordingly, by the moment the temperature region where the β-modification would have to be formed is reached, the specimen may have no more amorphous phase capable of crystallization.

It is this that causes the differences in the phase states reached by the "fast" and "slow" cooling of the melt, and shown by the scheme presented. That is why investigations on specimens crystallized isothermally at fixed temperatures seem to be more definite and hence more informative, insofar, of course, as it is possible to speak of "isothermality", bearing in mind the characteristic features of the thermokinetics of polymer crystallization mentioned above.

Experimental

A sample of the earlier-investigated PEA of $\overline{M}_n \approx 2000$ was used [2, 3, 10]. The amorphization was achieved by heating a specimen of 50 mg in the micro-testing tube with the mounted thermocouple for 10 min in an oil bath of appropriate temperature (80° unless otherwise indicated). After this, in one series of experiments the tube was immediately inserted into liquid nitrogen for quenching, and in another into a thermostat for crystallization. In a certain series the amorphized specimens were first quenched, and only then put into the thermostat. The duration of tempering usually varied from 10 to 120 min. The specimens prepared were immediately placed into the pre-cooled thermal block of the DTA set.

The DTA curves were obtained with a recorder of the ПДС-021 type and an amplifier of the И-37 type. The heating of the thermal block was linear, the discrete rates ranging from 1.7 to 7.7 degree $\cdot$ min^{-1}. For most of the curves the rate was 2.5 degree $\cdot$ min^{-1}. The temperatures were estimated with an accuracy of ±1°.

Results and discussion

Amorphized specimens

The usual kink in the glass transition region, exothermic crystallization peaks close to the glass temperature and prior to melting, and an endothermic peak of melting are to be observed in the DTA curves of amorphized PEA (Fig. 1, a).

The very sharp low-temperature peak indicates that the crystallization process, starting from some threshold temperature, proceeds with self-promotion. The broad distance between this crystallization peak and the melting peak is accounted for by the fact that the actual crystallization temperature (when the process is fast enough) appears to be much higher than the nominal one read on the temperature scale against the foot of the proper peak [5]. The self-heating due to evolution of the crystallization heat for PEA was recently shown to reach at least 40° [11].

When the crystallization process is over, the polymer cools rapidly, approaching the temperature of the cold thermal block. Melting of the polymer during the DTA is unable to start before the specimen is again heated (this time with the block) to the actual temperature of its crystallization. However, the endothermic melting peak is preceded by the second exothermic peak mentioned, the nature of the latter being a matter of special interest.

Such a peak is explainable, if not by polymorphic transition, then by the possibilities arising for crystallization of part of the amorphous material, trapped and immobilized by the crystal structures previously formed [12].

A similar interpretation has been adopted by us for PEA too [3, 7]. However, there is no apparent need for a figurative representation of "trapping". It is sufficient to bear in mind that the crystallization process terminates because of the decrease in mobility of the macromolecules, and thus a definite amorphous-to-crystalline phase ratio is reached, which is characteristic of a given polymer at a given temperature. In other words, the crystallization of a polymer may proceed up till the complete loss of mobility of the amorphous parts of the chains. Hence, the actual crystallization temperature becomes the glass temperature for the amorphous part of the polymer.

The cooling of such a specimen would not change the degree of crystallinity reached. Indeed, decrease of the intensity of thermal mobility makes transitions between the amorphous and crystalline phases of the polymer ultimately crystallized still more kinetically hindered.

In contrast, with increasing temperatures its degree of crystallinity cannot, in principle, remain constant. At one and the same time the glassy amorphous part will undergo softening and the crystalline one will begin to melt, both processes giving rise to re-crystallization. It is well-known that in order to perfect the crystalline structure (in other words, to increase the degree of crystallinity) polymers are annealed at temperatures higher than that of crystallization. Now it is easy to understand that the annealing will be efficient only at temperatures higher than the actual (and not the nominal) crystallization temperature.

All the above enables us to explain the peculiarities of the DTA curves of PEA as well as of some other polymers exhibiting an exothermic maximum prior to melting. The crystallization, beginning at low temperatures, very soon comes to a certain limit corresponding to the highest temperature reached. As has been noted, in the further run of the DTA experiment the temperature first drops and then rises again. No alteration in the degree of crystallinity occurs till the specimen once again reaches the temperature at which the crystallization proceeded. Having exceeded this, however, the polymer begins to melt and re-crystallize, so that the degree of crystallinity may increase, approaching a new value characteristic of a higher temperature.

It is worth emphasizing that melting and re-crystallization do not appear as different consequent stages of the change of the polymer state. Both processes proceed simultaneously, so that a kind of dynamic equilibrium between the amorphous and crystalline phases is maintained. At any temperature point this depends on the relation of the melting velocity (set by the crystallization temperature spectrum as well as by the heating rate*) and of the re-crystallization velocity.

As follows from the aforementioned, crystallization terminated at a certain actual temperature can proceed further as soon as the crystallized polymer is heated above this temperature. It is this process to which the second exothermic DTA peak corresponds (Fig 1, a). The beginning of the exothermic elevation may serve as an indication of the actual temperature of the original crystallization (and equally of the beginning of the melting and re-crystallization processes). The temperature range of the peak in question, in which the additional crystallization occurs, appears to be a continuation of the actual temperature range of primary crystallization. That is why the melting of the crystals formed in both of these stages proceeds successively, so that no endo-peak splitting is observed.

All that has been said on the two crystallization stages may also be observed for specimens crystallized not in the dynamic regime of DTA, but by tempering (see below). The situation formally resembles that often observed in radical polymerization research: a reaction, terminated at a given temperature, proceeds further and reaches a higher degree of conversion when heated to more elevated temperatures.

The DTA curves obtained for the amorphized PEA with various heating rates are not given here; they are all of the same type. However, it is characteristic that with the increase of rate the beginning of the first exothermic peak shifts over to higher temperatures (the difference for the extreme rates used was as high as 10 – 12°), whereas the positions of the second exo-peak and the melting peak remain constant.

The shift of the low-temperature peak seems to be natural and is easily explained. At high heating rates a more elevated temperature is required for the crystallization process to reach (in a shorter period of time) the self-promotion threshold to which the sharp elevation of the DTA curve corresponds.

The position of the second exo-peak being independent of the heating rate confirms the validity of the concepts developed on the low-temperature crystallization thermokinetics. Though the threshold temperatures mentioned are different, the process at the self-promotion stage does not depend upon the outward heat transport and always reaches one and the same temperature. As will be shown later, the latter is the optimum crystallization temperature.

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* For some polymers at high rates over-heating must also be taken into account [18].

The shape of the DTA curve in Fig. 1, a is the same, irrespective of the temperature of the melt before quenching: 60, 70, 80, 90 or 100°. Each of these temperatures ensures full melting of the PEA. Quite another result is obtained for a specimen heated only to 50° prior to quenching, which is insufficient for full melting of the PEA (Fig. 1,b). Crystals re-crystallized at this temperature, and some melt, are present in such a specimen.

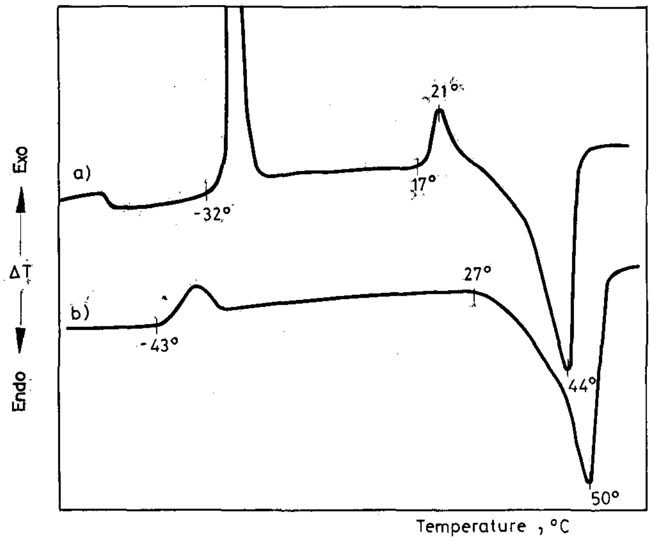


Fig. 1. DTA of amorphized PEA. Prior to the experiment the specimen was heated for 10 min: a) at 60° (complete melting; similar curves are obtained when heated at more elevated temperatures); b) at 50° (incomplete melting). After heating the specimens were quenched with liquid nitrogen

Fig. 1, b shows a small exothermic peak, corresponding to the crystallization of this melted part in the DTA run.

It is worth noting that this time the crystallization begins at a temperature lower than in the case of the fully amorphized PEA. This may be explained by the presence of the crystalline phase, due to which no primary nucleation stage is necessary. A similar exo-peak has also been found for other polymers [13]. However, this was followed by an endo-peak of about the same size at temperatures lower than those of the main melting peak. There is no such endo-peak for PEA (Fig. 1,b).

It is hardly possible that during the crystallization of a relatively small mass of the amorphous material the actual crystallization temperature immediately reaches the magnitudes corresponding to the main melting peak. It seems more probable to assume that the crystals formed at the exo-peak melt near the peak, but, due to the high crystallizability of the PEA, immediately and successively re-crystallize, reaching the state corresponding to the main melting peak. Naturally, due to such a re-crystallization route the DTA curve does not exhibit a pre-melting maximum.

Specimens crystallized from the melt

There is no low-temperature crystallization peak in the DTA curves of crystallized specimens. This appears only when the duration of tempering is insufficient and not all the amorphous mass capable of crystallization has been crystallized. The lowest duration required is temperature-dependent. This having been attained, no extra exposure changes the general shape of the DTA curves.

In the course of crystallization from an over-cooled melt, crystals appear with a more or less broad spectrum of the actual formation temperatures, and consequently of the non-recrystallization melting temperatures, even under tempering conditions [5]. This spectrum in a general case extends from the highest actual temperature reached during crystallization to the thermostat temperature. That is

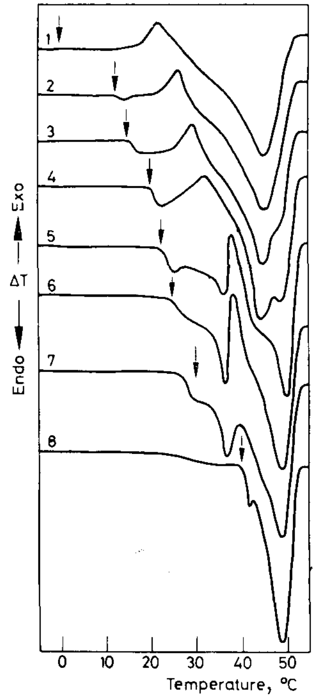


Fig. 2. DTA curves of PEA crystallized from the melt (80°) by tempering. The temperatures of the thermostat (°C) are indicated by arrows: 1 — 0 (as well as −25 and −10°), 2 −12.5, 3 −15, 4 −20, 5 −22.5, 6 −25, 7 −30, 8 −40

why the melting of a polymer often (but not always) starts at a point of the DTA curve corresponding to the temperature of the thermostat, i.e. the nominal crystallization temperature.

At very high crystallization rates the bulk of the crystals are formed by maximum self-heating, and in the spectrum mentioned no crystals are formed near the nominal crystallization temperature. In this case the DTA curves cannot exhibit any signs of the melting starting at the point of tempering. Experiments confirm the above considerations.

The DTA curves of PEA crystallized at various temperatures (Fig. 2) are generally characterized by different shapes in the melting region. For all the specimens tempered at 10° and higher, the curves recorded from lower temperatures (Fig. 2, 2 and the next) exhibit a more or less marked lowering of the curve at the point of tempering, which indicates the beginning of melting. For PEA tempered at temperatures below those mentioned above (-25, -10 and 0°), however, the DTA curves (Fig. 2, 1) do not exhibit any singularities at these temperatures, and there are no deflections till the beginning of the exothermic elevation. For all the low-temperature specimens studied, as well as for the amorphized PEA, this is one and the same temperature of about 15°. Such a non-dependence of the position of the pre-melting peak (and the melting peak as well) upon the temperature of tempering has also been observed for another polyester [1].

We must conclude that, in spite of the different temperatures of tempering, the self-promoting crystallization process actually proceeds in these cases at the optimum temperature. Surpassing the latter would lead to the inhibition of the process and hence to some lowering of the temperature reached.

The existence of such reversed feedback results, in the case of rapidly crystallizing polymers, in maintaining the level of the maximum actual crystallization temperature (only when the bulk of the polymer becomes crystallized may the process begin to decrease in speed and will its last stages proceed at lower temperatures).

The maximum level, however, in contrast to that known for non-polymeric crystallizable materials, is still much lower than the thermodynamic equilibrium value, and crystallization (with a lesser velocity) may occur at temperatures higher than the optimum one. The heat evolution at these temperatures contributes to the slowing-down of the process, rather than its acceleration, and thus the self-heating in fairly moderate.

In a definite temperature interval the reverse feedback mechanism contributes, as has been shown [14], to the appearance of a specific periodic (ringed) spherulitic structure. For PEA the interval is from 20° to 40°. The heat evolution at the periphery of a spherulite growing in the over-cooled melt results in the periodic inhibition and acceleration of the process, so that layers of lower and higher actual crystallization temperatures are repeatedly formed. The crystallites have different orientations in the layers, and for PEA of the molar weight investigated their structures were identified as the β- and α-forms.

The distance between any two neighboring rings in the real PEA ringed spherulites is about $5 \cdot 10^{-4}$ cm. This leads to the conclusion that in general the heat dissipation from a growth site of a polymer crystal also extends in space with the same order of linear dimensions. Hence, the whole thermokinetics under consideration are related to the microscopic regions of the polymer, so the size of the specimen as a whole cannot markedly affect the real crystallization temperature. At the same time the temperature of the crystallizing specimen which is macroscopically measured (as well as the difference of the specimen and reference temperatures in the DTA) will obviously be the higher, the greater the mass of the specimen and the more the heat transfer is hindered.

On elevation of the tempering temperature up to 20°, the DTA curves (Fig 2, 2–4) slightly transform, the temperature of the exo-peak gradually increasing, but the curves in general maintaining their shape. Further elevation of the temperature of tempering, however, even up to as low as 22.5°, leads to a very sharp alteration of the shape of the whole curve. We consider this to be linked with change of the crystallization morphology in this temperature interval, i.e. with the formation of the ringed spherulites. Two distinct melting regions prior to the DTA exo-peak (Fig. 2, curve 5) may be assigned to the beginning of melting of the low- and high-temperature layers, respectively. Moreover, the existence of these two stages of melting may be regarded as evidence in favour of the above mechanism of formation of ringed spherulites. It may be noted that the problem of the structure and ways of formation of these spherulites is still a subject of discussion.

The initial parts of the curves (Fig. 2) deserve particular attention. The segments of the relatively sloping elevation (curves 2–4) or lowering (curves 5–7) after the beginning of melting are characteristic of partial mutual compensation of the melting and re-crystallization processes. If the compensation were complete, the segment would be strictly horizontal and one could speak of "equilibrium" re-crystallization. One of the processes usually prevails.

The pre-melting crystallization of specimens tempered at 22.5, 25 and 30°, having ringed spherulite morphology, is expressed by a sharp exothermic elevation of the DTA curves at one and the same temperature of about 36–40°. From these temperatures onwards the crystallization of the PEA mostly proceeds in the α-form. Here, the crystallization process involves both the amorphous parts which remained uncrystallized from the very beginning, and those which arose during the melting.

As a result, a significant part of the PEA undergoes re-crystallization at about 40°, this being reflected in the further run of the DTA curves. The final melting of such specimens proceeds at temperatures markedly higher (endo-peak at 50°) than those of the specimens which undergo re-crystallization at lower temperatures (peak at about 45°). In the intermediate cases the final melting peak appears to be double; two minima or a minimum and a shoulder are observable. The shoulder corresponds to the type of crystals present in lesser amount; it passes from the right branch of the peak to the left one with increase of the crystallization temperature.

However, the relationship between the PEA dimorphism and the melting peak splitting is not unique. Quite similar results are obtainable if crystals of one and the same modification but of different formation temperatures were present in the specimen.

For dimorphic non-polymer substances both equilibrium or metastable melting points are unambiguously determined by the crystalline structure: the crystals of each of the modifications melt at different, rigidly definite temperatures. In the case of polymers the melting point of every crystallite is set by its actual temperature of formation, determining its degree of perfection.

Differences in the melting points due to various degrees of perfection of the polymer crystallites may well surpass the differences caused by their being unlike modifications. The less perfect crystalls of the higher equilibrium melting point form may melt at temperatures lower than the crystals of the low-temperature form but crystallized to a greater perfection. This is termed thermodynamic stability inversion [8].

Hence, in the case of PEA it would be incorrect to state that the first minimum (or shoulder) fully corresponds to the β-form melting, and the second minimum (or shoulder) to the α-form. It is more correct to consider that in the first peak mainly the β-form crystals actually melt, but the less perfect crystals of the α-form melt here too. As for the second one, the bulk of the α-form crystals melt here, as well as the most perfect crystals of the β-form. Indeed, it has been shown earlier that the β-form fully disappeared only at 46° [3].

For the PEA specimen crystallized at low temperatures in the β-form no double melting peak is to be found, in spite of its transition to the α-form which may occur in the course of heating above 36°. This transition proceeds smoothly, one modification being replaced gradually and only partially by the other (against a background of progressive melting).

With regard to the results obtained it is necessary once again to emphasize that when bimodality is present in the actual crystallization temperature spectrum (no matter whether it is due to polymorphism or to some other reason) it will inevitably show up in the DTA as a double melting peak, even with re-crystallization present. As a rule the latter cannot fully level off the behaviour of the crystals formed at different temperatures. For each of them the re-crystallization follows its own pathway, so that the states reached by them at a certain point appear to be different.

It is also necessary to remember that the above refers to the thermal regime of the DTA. When re-crystallization proceeds long enough at any constant temperature during annealing, the spectrum under consideration will lack crystals which would have their temperature of formation lower than the annealing one. All these crystals will re-crystallize to one and the same level. That is why the PEA of ringed spherulitic morphology annealed e.g. at 40° exhibits no signs of the two melting stages, though retaining its initial morphology.

The problem of the re-crystallization mechanism is not considered here. Two ultimate mechanisms are discussed in the literature. The first one is when some crystallites undergo melting, and some others, more perfect, are formed from the melt (re-crystallization proper). The second one is the perfection of the crystallites which proceeds in the solid state, in no way involving the melt ("re-organization").

We consider it hardly possible to separate the two mechanisms for polymers, as crystalline polymers always contain a considerable amount of amorphous material, that is to say of the melt. The thing to be discussed is the location, or to be more precise, the partition of this amorphous mass, i.e. what part of it is represented by the defects of the crystal structure (it might be connected with the re-organization concept), and what part of it forms an interstructure phase. Thermal analysis alone is evidently insufficient for solving this problem. At any rate, the investigation presented here seems to indicate that the explanation of the multiplicity of the DTA melting peak does not require any assumptions [15, 16] on the separate actions of the two mechanisms mentioned.

Specimens crystallized after quenching

The quenching tells little on the DTA curves (Fig. 3, 1) for specimens crystallized at relatively low temperatures (below 12.5°). Significant differences appear for

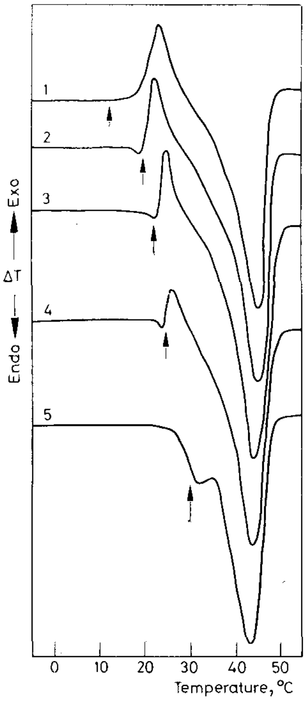
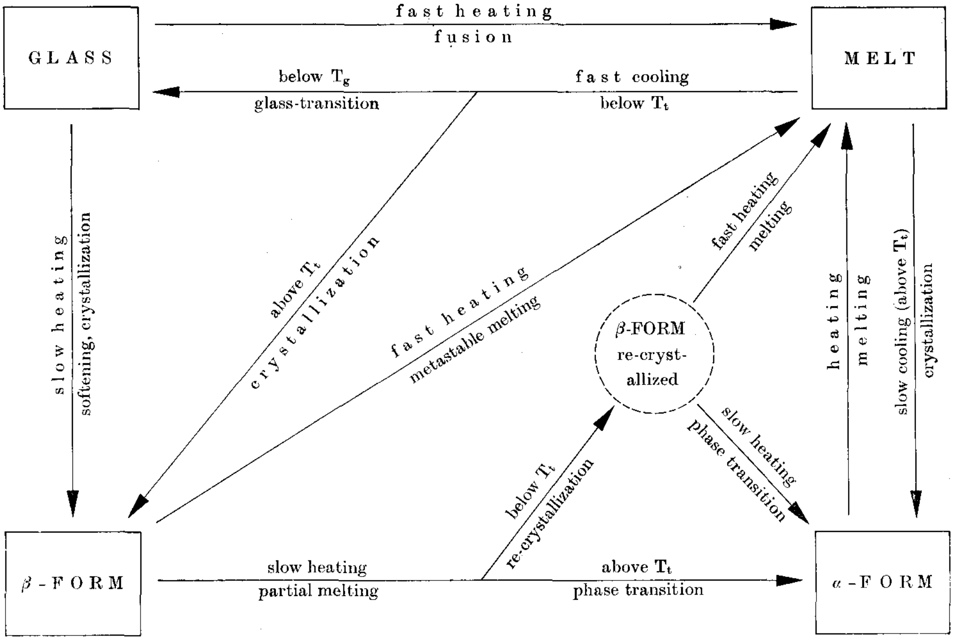


Fig. 3. DTA curves of PEA undergoing tempering after preliminary quenching of the melt (80°) with liquid nitrogen. The temperatures of the thermostat (°C) are indicated by arrows: 1 —12.5 (as well as 0°), 2 —20, 3 —22.5, 4 —25, 5 —30

PEA crystallized at higher temperatures (curves *2–5*). The picture always tends to be simpler for the quenched specimens.

The reason for the dissimilarity of the quenched and unquenched (Fig. 2) specimens is the non-identity of the crystalline structures formed, which depends on the differences in nucleation. Crystal growth in unquenched PEA at a not very low temperature proceeds on a relatively few nuclei in the melt, brought to crystallization temperature from the higher-temperature direction. Rather large spherulites form.



STATE TRANSITION SCHEME FOR A MONOTROPIC (OR A PSEUDO-MONOTROPIC) POLYMER

T_g is the glass temperature, T_t the $\beta \rightarrow$g transition temperature

Crystallization of the quenched specimens takes quite another course. Here crystal growth proceeds far away from the temperature given, when nearing it from the low-temperature side, in just the same manner as was observed in the DTA of amorphized PEA. Under such conditions the crystallization proceeds extremely quickly around a multitude of centers, so that a characteristic microcrystalline structure is formed.* Upon reaching the tempering temperature the crystals formed have only to recrystallize.

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* The high crystallization rate of quenched PEA is evident from the fact that the DTA curves show the specimen to have reached the maximum crystallinity even in experiments with the least duration of tempering, which was not always observed for unquenched specimens.

It is this temperature on the DTA curves, from which melting proceeds. To be exact, the first signs of melting are to be noticed a few degrees below, as a tiny endopeak preceding the exotherm. However, this is only evidence of some rather imperfect (more defect) crystals, having a relatively lower melting point, which remain after re-crystallization.

As already mentioned, the re-crystallization of PEA below the transition point $\beta \rightarrow \alpha$ (36°) [3, 17] proceeds without any polymorphic transition. That is why the quenched specimens appear to be crystallized as the β-form at all the nominal temperatures investigated, those at which unquenched specimens form the ringed spherulites with the complex phase structure among them.

This is the reason for the relative simplicity of the DTA curves obtained. Even the pre-melting crystallization does not complicate the melting peak. This process occurs in the temperature region close to the tempering point, so the main melting peak does not exhibit any multiplicity. It is important to note that to obtain the quenching effect no extreme cooling of the specimen is necessary, for instance by means of liquid nitrogen, as in the above experiments. Quite identical results are obtainable, if the PEA specimens are tempered twice: the first time at a lower, the second at a higher temperature (-25 and $+15$, or -15 and $+20$, and so on).

Preliminary crystallization at a low temperature does not make the curves exhibit the rather complex shape they would have if the PEA were crystallized from the melt only at the higher of the temperatures. The re-crystallization of the crystals previously formed, proceeding on the second tempering, shifts the beginning of their DTA melting to the level of this tempering.

There can be no doubt that the approach used in this paper for the interpretation of the DTA curves of PEA may be of use for investigations of other crystalline polymers as well.

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References

1. B. YA. TEITELBAUM and L. L. TUZOVA, Vysokomolekul. Soedin., A-15 (1973) 917.
2. B. YA. TEITELBAUM and N. A. PALIKHOV et al., Vysokomolekul. Soedin., A-9 (1967) 1672.
3. B. YA. TEITELBAUM, V. I. KOVALENKO and N. A. PALIKHOV, Sintez i fizikokhimiya polimerov, Kiev, 1971, p. 55.
4. B. YA. TEITELBAUM, V Vsesoyuznoe sovestshanie po termicheskomu analizu, Novosibirsk, 1973. Tezisy dokladov, Moscow, 1973, p. 19.
5. B. YA. TEITELBAUM, Vysokomolekul. Soedin., B-16, (1974) 763.
6. B. YA. TEITELBAUM, IV. International Conference on Thermal Analysis, Budapest, 1974. Abstracts of papers, p. 177.
7. B. YA. TEITELBAUM, Doklady Akademii Nauk SSSR, 181 (1968) 368.
8. F. DANUSSO, Polymer, 8 (1967) 281.

9. W. C. McCrone, In Physics and Chemistry of the Organic Solid State, Eds. D. Fox et al. New York—London—Sydney. Interscience publ., T. 2, 1965, p. 725.
10. B. Ya. Teitelbaum and N. P. Anoshina, Vysokomolekul. Soedin., B-10 (1968) 26.
11. B. Ya. Teitelbaum and N. P. Anoshina, Vysokomolekul. Soedin., A-16 (1974) 682.
12. H. E. Bair and R. Salovey, J. Polymer Sci., B-5 (1967) 429.
13. B. Ya. Teitelbaum and N. P. Anoshina, Vysokomolekul. Soedin., 7 (1965) 978.
14. B. Ya. Teitelbaum and N. A. Palikhov, Vysokomolekul. Soedin., B-12 (1970) 3.
15. I. V. Sochava, Fizika Tvyordogo Tela, 15 (1973) 1559.
16. I. V. Sochava and O. I. Smirnova, Fizika Tvyordogo Tela, 15 (1973) 3003.
17. V. P. Privalko, Vysokomolekul. Soedin., A-14 (1972) 1235.
18. E. Hellmuth, B. Wunderlich, J. Appl. Phys. 36 (1965) 3093.

Résumé — A la lumière des idées développées sur les particularités cinétiques de la cristallisation des polymères, on donne une interprétation des caractéristiques des courbes ATD du poly(éthylène adipate) complexe. On a étudié les échantillons à l'état amorphe, dont la cristallisation se produit pendant l'expérience d'ATD, ainsi que ceux qui avaient été précristallisés par maintien du produit fondu à des températures données. L'état du polymère cristallisé diffère essentiellement suivant que la température de cristallisation est atteinte en partant d'une température qui lui est supérieure ou inférieure. D'après les résultats d'analyse thermique, on conclut qu'il faut tenir compte de l'inégalité des températures de cristallisation nominales et effectives ainsi que de la recristallisation.

Zusammenfassung — Eine Deutung aller Elemente der DTA-Kurven komplexer Poly-(Äthylen-Adipate) wird unter Berücksichtigung der Vorstellungen über die Beschaffenheit der Thermokinetik der Polymerkristallisation gegeben. Sowohl die amorphen, während der DTA kristallisierenden, als auch die bei einer bestimmten Temperatur durch Härtung der Schmelze vorkristallisierten Substanzen wurden untersucht. Die Zustände des kristallinen Polymeren unterscheiden sich wesentlich wenn die Kristallisationstemperatur von einer höheren oder einer niedrigeren Temperatur her erreicht wird. Unter Berücksichtigung der Ergebnisse der Thermoanalyse wird gefolgert, daß die Ungleichheit der nominellen und der tatsächlichen Kristallisationstemperaturen sowie Rekristallisation beachtet werden müssen.

Резюме — В свете развиваемых представлений об особенностях термокинетики кристаллизации дана интерпретация всех элементов ДТА-кривых полиэтиленадипината — как аморфизованного (кристаллизующегося в ходе регистрации кривых), так и предварительно закристаллизованного путем термостатирования при фиксированных температурах. Состояния закристаллизованного полимера существенно различаются в зависимости от того, приведен ли он к температуре кристаллизации со стороны низких или же высоких температур. Сделан вывод, что при обсуждении данных термического анализа должны быть приняты во внимание нетождественность номинальной и фактической температур кристаллизационные явления в ходе плавления.